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MP-1a: A CERTIFIED REFERENCE ORE

H.F. STEGER AND W.S. BOWMAN

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MINERAL SCIENCES LABORATORIES

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MP-1a: A Certified Reference Ore

by

H.F. Steger* and W.S. Bowman**

SYNOPSIS

A 345-kg sample of a base metal ore from Mount Pleasant, New Brunswick, has been prepared as a compositional reference material to replace the similar certified ore, MP-1, of which the stock had been exhausted. MP-1a was ground to minus 74 µm and mixed in one lot. Approximately one half of this ore was bottled in 200-g units and tested for homogeneity with respect to its zinc and bismuth contents by chemical methods. The remaining material is being stored in bulk under periodic purging with nitrogen gas.

In a "free choice" analytical program, 21 laboratories contributed results for one or more of zinc, lead, copper, tin, arsenic, bismuth, indium, molybdenum, tungsten and silver in one bottle of MP-1a. Based on a statistical analysis of the data, the following recommended values were assigned: Zn, 19.02%; Pb, 4.33%; Cu, 1.44%; Sn, 1.28%; As, 0.84%; In, 0.033%; Bi, 0.032%; Mo, 0.029%; and Ag, 69.7 µg/g.

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Note: Major contributions were also made by other staff members of the Mineral Sciences Laboratories.

MP-1a: Minerai de Référence

par

H.F. Steger* et W.S. Bowman**

SYNOPSIS

Un échantillon de 345-kg de minerai de métaux communs provenant de Mount Pleasant au Nouveau-Brunswick a été préparé comme matériau de référence de composition pour remplacer le minerai certifié analogue, MP-1, dont l'inventaire avait été épuisé. Le MP-1a a été broyé à une granulométrie de moins 74 µm et mélangé en lot de minerai. Approximativement une moitié de ce minerai a été embouteillée en unités de 200-g et soumise à des essais d'homogénéité quant au zinc et bismuth par des méthodes chimiques. Le reste du matériau se met en réserve en gros avec une purge périodique avec du gaz d'azote.

En vertu d'un programme analytique de "libre choix", 21 laboratoires ont soumis les résultats pour un ou plusieurs des éléments suivants: zinc, plomb, cuivre, étain, arsenic, bismuth, indium, molybdène, tungstène et argent sur une bouteille du MP-1a. Suite à analyse statistique des données, les valeurs recommandées suivantes ont été assignées: Zn, 19,02%; Pb, 4,33%; Cu, 1,44%; Sn, 1,28%; As, 0,84%; In, 0,033%; Bi, 0,032%; Mo, 0,029%; et Ag, 69,7 µg/g.

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Nota: D'autres membres du personnel des Laboratoires des sciences minérales ont également apporté une grande contribution à ce projet.

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INTRODUCTION

The preparation, characterization and certification of base metal ore MP-1a is a further contribution of the Canadian Certified Reference Materials Project (CCRMP) in its endeavour to provide compositional reference ores, concentrates and related products typical of Canadian deposits and generally unavailable from other sources for use in analytical laboratories associated with mining, metallurgy and the earth sciences. Other certified reference materials are described in a catalogue available from CANMET, Energy, Mines and Resources, Ottawa, Canada (1).

MP-1a is intended to replace MP-1, the supply of which was exhausted (2,3). MP-1 was certified in 1972 for zinc, lead, copper, tin, arsenic, bismuth, molybdenum, indium and silver. Only a provisional value for tungsten was given. MP-1a was prepared with a higher tungsten content to provide a better chance for certification for this element. MP-1 had been a popular reference material because of the large number of certified elements and because of its mineralogical complexity.

An interlaboratory program was conducted to obtain results for 10 elements from 21 commercial, industrial and government laboratories using analytical methods of their choice. The results should therefore be indicative of the state-of-the-art of the analysis for these elements.

NATURE AND PREPARATION

The two raw materials which were blended to make MP-1a were donated to CCRMP in October 1978 by Billitone Exploration Company Limited and are representative of the sulphide and of the wolframite-molybdenite-bismuth mineralization deposits at Mount Pleasant, New Brunswick. The materials were hand-picked at the mine site by CANMET geologists (4).

Both samples were dry-ground in March 1980 to pass a 74-µm screen. The powdered ore, consisting of 330.5 kg of the high sulphide-bearing material and of 14.5 kg of the wolframite-molybdenite-bismuth-bearing material, was tumbled in a 570-L conical blender for 8 h. Approximately one half of the blended material was bottled in 200-g units which were heat-sealed in polyester-aluminium foil-polyethylene pouches to prevent oxidation while in storage at CANMET. The remainder of the material is being stored in bulk under periodic purging with nitrogen gas.

The analysis of 15 randomly-selected bottles of MP-1a for both zinc and bismuth demonstrated the material to be sufficiently homogeneous for use as a reference material. The results of the evaluation of the homogeneity of MP-1a are reported in Appendix A.

The approximate mineralogical and chemical composition and the particle size analysis are given in Tables 1 to 3.

Table 1 - Approximate mineralogical composition

Mineral	wt %
Quartz	36.5
Sphalerite	31.6
Chlorite	9
Galena	4.9
Chalcopyrite	4.1
Arsenopyrite	4.0
Topaz	4
Fluorite	2
Cassiterite	1.5
Kaolinite	1
Pyrite	0.7
Stannite	0.5
Rutile	0.5
Lepidocrocite	0.2
Molybdenite	0.04
Wolframite	0.04
Loellingite	0.04
Calcite	0.04
Bismuthinite	0.03
Bismuth	0.01
Tennantite	0.01
Monazite	0.004
Zircon	0.004

Table 2 - Approximate chemical composition

Element	wt %*
Si	19.4
Zn	19.02
S	12.8
Fe	6.2
Al	5.2
Pb	4.33
F	2.2
Ca	2.1
Cu	1.44
Sn	1.28
As	0.84
W	0.040
Mo	0.029
In	0.033
Bi	0.032
C (total)	0.03
Mg	0.02
Ag	69.7 µg/g
H_2O (105°)	0.01

*Mean of minimum of two determinations or certified value.

Table 3 - Particle size analysis (wet screen)

Size of fraction (µm)	wt %*
-104 + 74	0.2
-74 + 55	12.2
-55 + 46	3.4
-46 + 37	9.4
-37	74.8

*Mean of duplicate determinations

INTERLABORATORY PROGRAM FOR CERTIFICATION

The laboratories that participated in the certification program are listed in Appendix B. Each was assigned a code number which bears no relation to its alphabetical order. The results from CANMET are reported as Laboratories 30, 51, 52 and 53.

To prevent the situation wherein nearly all laboratories would submit results for elements such as zinc, lead, copper, etc., but where only a few would submit results for indium, bismuth, tungsten, etc., CCRMP divided the elements into three groups:

(1) zinc, lead, copper, tin
(2) arsenic, tin and
(3) bismuth, indium, molybdenum, tungsten

and requested each participating laboratory to state which elements in each group it preferred to analyze for. An attempt was made to assign to as many laboratories as possible their two preferred elements from groups (1) and (3) and one preferred element from group (2) and still ensure a sufficient number of results for each element to permit certification by consensus.

Each laboratory was requested to contribute five replicate results for the assigned elements for one bottle of MP-1a by methods of its own choice and to report the results on an "as is" basis. Some laboratories however deviated from the request for five results for an element or contributed results for more than five elements. When a laboratory submitted results by more than one method for an element, each set was considered statistically independent.

The recommended values for MP-1a are presented in Table 4. Methodological and analytical information is presented in Tables 5 and 6.

STATISTICAL TREATMENT OF ANALYTICAL RESULTS

DETECTION OF OUTLIERS

Any sets of results obviously suspect for methodological reasons were rejected. Also, the sets of results whose means differed by more than twice the overall standard deviation from the initially calculated mean value were not used in subsequent computations to avoid biasing of the statistics. All results that were rejected are identified in Table 6.

ESTIMATION OF CONSENSUS VALUES AND 95% CONFIDENCE LIMITS

A one-way analysis of variance technique was used to estimate the consensus value and vari-

Table 4 - Recommended values and statistical parameters (outliers excluded)

Element	No. of laboratories	No. of results	Overall mean	95% CL Low	95% CL High	σ_A*
			wt %			
Zn	15	95	19.02	18.91	19.12	0.10
Pb	16	105	4.33	4.30	4.36	0.02
Cu	18	125	1.44	1.43	1.44	0.01
Sn	10	80	1.28	1.25	1.32	0.02
As	14	84	0.84	0.82	0.86	0.01
In	6	50	0.033	0.032	0.034	0.0008
Bi	10	65	0.032	0.030	0.034	0.0008
Mo	14	80	0.029	0.028	0.030	0.0006
Ag	14	90	69.7	67.9	71.4	1.1

*Average within-set standard deviation.

ance. This approach considers the results of the described certification program to be only one sampling out of a universal set of results. The analytical data were assumed to fit the model (5).

$$x_{ij} = \mu + y_i + e_{ij}$$

where x_{ij} = the j^{th} result in set i,
μ = the true consensus value,
y_i = the discrepancy between the mean of the results in the set i ($\bar{x}_i.$) and μ, and
e_{ij} = the discrepancy between x_{ij} and $\bar{x}_i.$

It is assumed that both y_i and e_{ij} are normally distributed with means of zero and variances of ω^2 and σ^2, respectively. The significance of ω^2 is detected by comparing the ratio of between-set mean squares to within-set mean squares with the F statistic at the 95% confidence level and with the appropriate degrees of freedom.

The consensus value of the assumed model is estimated by the overall mean $\bar{x}..$ by:

$$\bar{x}.. = \sum_i^k \sum_j^{n_i} x_{ij} \Big/ \sum_i^k n_i$$

where n_i = the number of results in set i, and
k = the number of sets.

The value of σ^2 is estimated by s_1^2 which is given by

$$s_1^2 = \sum_i^k \sum_j^{n_i} (x_{ij} - \bar{x}_i.)^2 \Big/ \sum_i^k n_i - k.$$

The value of ω^2 is estimated by

$$\omega^2 = (s_2^2 - s_1^2) \Big/ \frac{1}{k-1}\left(\sum_i^k n_i - \sum_i^k n_i^2 / \sum_i^k n_i\right)$$

where

$$s_2^2 = \sum_i^k n_i (\bar{x}_i. - \bar{x}..)^2 \Big/ k-1.$$

The variance of the overall mean is given by

$$V[\bar{x}..] = \left(\sum_i^k n_i^2 / (\sum_i^k n_i)^2\right) \omega^2 + \left(1/\sum_i^k n_i\right)\sigma^2$$

and the 95% confidence limits for $\bar{x}..$ are

$$\bar{x}.. \pm t_{0.975,\,(k-1)} \sqrt{V[\bar{x}..]}$$

To avoid giving an unduly heavy weighting to the contribution for zinc and bismuth from CANMET, only five results for each were selected at random out of the 45 available from the evaluation of the homogeneity of MP-1a.

Table 5a - Summary of analytical methods for zinc (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + one or more of HCl, HF, $HClO_4$, H_2SO_4; 1-3M HCl	5, 11a, 12a, 19, 26a	25	18.98
	HF to dryness; taken up in HNO_3 + HCl + $HClO_4$	15	5	19.16
	HNO_3; 5% HNO_3 in final solution	7	5	19.08
	$HClO_4$; 5% HCl in final solution	18, 28	10	19.31
Titrimetry	HNO_3 + one or more of HCl, HF, $HClO_4$; dissolved in	CANMET (2), 11b	30	19.05
	HCl + H_2SO_4; filtered off $PbSO_4$; separated Zn as thiocyanate by MIBK extraction; titrated with EDTA	12b, 14b, 23		
	HNO_3 + HCl + HF + H_2SO_4; separated Re_2O_3; reduced with lead shot; titrated with ferrocyanide using ammonium molybdate as indicator	9, 26b	10	19.06
ICP-emission spectrometry	HNO_3 + HF + $HClO_4$; residue fused with Na_2O_2; dissolved in 50% HCl	14a	5	18.56
X-ray fluorescence	Fused with $K_2S_2O_7$; ground and pressed into pellet	4	5	18.6

Table 5b - Summary of analytical methods for lead (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + one or more of HCl, HBr, HF, $HClO_4$, H_2SO_4; final solution was dilute HNO_3 or HCl	11, 12a, 15, 17, 19 24,26a	35	4.30
	HNO_3 + HCl + HF + $HClO_4$; tin and arsenic volatilized by HBr; $PbCO_3$ co-precipitated with hydrous iron oxide by $(NH_4)_2CO_3$ + NH_4OH; $PbCO_3$ filtered and dissolved in dilute HNO_3	CANMET (2)	10	4.30
	HNO_3 + HF; residue fused with Na_2O_2 + NaOH; final solution was 5% HCl	2	5	4.41
	HNO_3; residue fused with $LiBO_2$; final solution was 5% HNO_3	13	5	4.29
	Fused with Na_2O_2; taken up in 5% HCl	3	5	4.35
	HNO_3; final solution was 5% HNO_3	7	5	4.33
	$HClO_4$; final solution was 5% HCl	18, 28	10	4.39
Titrimetry	HNO_3 + HCl + HF + Br_2 + H_2SO_4; $PbSO_4$ filtered and dissolved in acetate medium; lead precipitated as chromate; filtered and dissolved in dilute HCl; KI added and I_2 titrated with $Na_2S_2O_3$	12b, 14b	10	4.32
	HNO_3 + HCl + HF + $HClO_4$; lead precipitated as $PbSO_4$; filtered and dissolved in HCl + NaCl and complexed with hexamethylene tetramine and titrated with EDTA	CANMET	5	4.50
	HNO_3 + HCl + HF + H_2SO_4; $PbSO_4$ filtered and dissolved in ammonium acetate; titrated with ammonium molybdate using tannic acid as indicator	26b	5	4.31
ICP-emission spectrometry	HNO_3 + HF + $HClO_4$; residue fused with Na_2O_2; final solution was 50% HCl	14a	5	4.37
X-ray fluorescence	Fused with $K_2S_2O_7$; ground and pelletized	4	5	4.25

Table 5c - Summary of analytical methods for copper (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Titrimetry	HNO_3 + HCl + HF + Br_2 + H_2SO_4; $PbSO_4$ filtered and was dilute HCl or HNO_3	3, 12a, 13b, 15, 16, 19, 23, 24, 26a	10	4.32
	HNO_3 + HCl + HF + $HClO_4$; HBr to volatilize tin and arsenic, residue fused with Na_2CO_3; final solution was dilute HCl	CANMET (2)	10	1.44
	HNO_3; residue fused with $LiBO_2$	13a	5	1.43
	HNO_3 + HBr	11a	5	1.46
	HNO_3 + HF; residue fused with NaOH + Na_2O_2	2	5	1.42
	HCl + HF + KNO_3	20	5	1.44
	HNO_3; final solution was 5% KNO_3	7	5	1.45
	$HClO_4$; final solution was 5% HCl	28	5	1.46
Titrimetry	HNO_3 + HCl + HF + H_2SO_4 and Br_2; fluoride, acetate and iodide added; titrated with $Na_2S_2O_3$	12b, 26b	10	1.44
	$HClO_4$; copper precipitated with $Na_2S_2O_3$; CuS digested and taken to dryness with HNO_3 + $HClO_4$; taken up with HCl; acetate added and titrated with $Na_2S_2O_3$	9, 11b	10	1.43
Colorimetry	HNO_3 + HCl + HF + H_2SO_4 to dryness; taken up in dilute HCl; copper determined as cuproine complex in n-amyl alcohol	CANMET	5	1.44
Electrolysis	HNO_3 + HCl + Br_2 + H_2SO_4; gravimetric electrolysis at 300 mV from tartrate and hydrazine solution	17	5	1.46
	$HClO_4$; gravimetric electrolysis from dilute HNO_3 + H_2SO_4	28	5	1.46
X-ray fluorescence	Fused with $K_2S_2O_7$; ground and pelletized	4	5	1.30

Table 5d - Summary of analytical methods for tin (outliers excluded)

Method	Decomposition, separation etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	Fused with Na_2O_2 + Na_2CO_3; taken up in HCl	12a, 17	10	1.36
	Fused with Na_2O_2 + Na_2CO_3; iron and tin separated as hydrous oxides; dissolved in dilute HCl	CANMET (2), 20b, 26	21	1.28
	Fused with Na_2O_2 + Na_2CO_3; taken up in dilute H_2SO_4; SiF_4 volatilized; tin extracted from 3M H_2SO_4 - 1.5M KI into toluene; back-extracted with 50% HNO_3 - 16% HCl; determined in 10% HCl - 0.5% tartaric acid	CANMET	5	1.27
	HNO_3 + HF; residue fused with NaOH + Na_2O_2; determined in 5% HCl	2	5	1.28
Titrimetry	Fused with Na_2O_2 + Na_2CO_3; iron and tin hydrous oxides separated; reduced with iron powder and titrated with potassium iodate	CANMET	5	1.25
	Fused with Na_2O_2; taken up in dilute HCl; reduced with aluminum powder and titrated with iodate	14a	5	1.43
X-ray fluorescence	1 g sample + 9 g of 1:1 KCl:SiO_2; pelletized	7	5	1.18
	No details	5, 20a	10	1.20
	Binder + internal standard pressed into pellets	4	4	1.24
ICP-emission spectrometry	HNO_3 + HF + $HClO_4$; residue fused with Na_2O_2 and leached with 50% HCl	14b	5	1.28
Colorimetry	Fused with Na_2O_2 + Na_2CO_3; taken up in dilute H_2SO_4; SnI_4 extracted and stripped with 2% NaOH; tin(IV) - gallein complex in n-amyl alcohol	12b	5	1.35

Table 5e - Summary of analytical results for arsenic (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + H_2SO_4; taken up in 25% HCl	12a	5	0.88
	Fused with KOH-MgO; taken up in 10% HCl; AsH_3 generated with $NaBH_4$	19	5	0.88
	Br_2 + HNO_3	16	5	0.894
Titrimetry	Acid digestion; $AsCl_3$ distillation; titrated with iodine	9, 26	10	0.806
	HNO_3 + H_2SO_4 + Br_2; $AsBr_3$ distilled; titrated with iodine	28	5	0.83
	HNO_3; KBr + hydrazine sulphate to dryness; taken up in HCl; $AsCl_3$ distilled and titrated with $KBrO_3$	12b	5	0.83
	HNO_3 + HCl; NaBr and hydrazine sulphate added; $AsBr_3$ distilled and titrated with $KBrO_3$ using Eriochrome SE as indicator	13	5	0.804
	Fused with $K_2S_2O_7$ + H_2SO_4; $AsCl_3$ distilled and titrated with $KBrO_3$	CANMET	5	0.83
Colorimetry	HNO_3 + HCl + H_2SO_4 + Br_2; As(V) co-precipitated with hydrous iron oxide; dissolved in 11M HCl and reduced to As(III) with Fe(II); arsenic extracted as xanthate into chloroform; oxidized by Br_2 and stripped into water; molybdenum blue complex	CANMET	5	0.775
	HNO_3 + H_2SO_4; arsenic extracted into chloroform - butanol as molybdenum blue complex	CANMET	5	0.85

Table 5e (cont'd)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
	HNO_3 + HF + $NaClO_3$ + H_2SO_4; arsenic extracted as iodide; determined as molybdenum blue complex	2	5	0.865
	HNO_3 + H_2SO_4; distilled as $AsCl_3$; molybdenum blue complex	17	5	0.80
	NaOH-Na_2O_2 fusion; AsH_3 generation; colour development using silver diethyldithiocarbamate in pyridine	24	5	0.90
ICP-AES	HNO_3 + HCl + $HClO_4$; taken up in 50% HCl; Te and HPO_2 added to precipitate arsenic; dissolved in HNO_3 + $HClO_4$	15	5	0.839
X-ray fluorescence	Sample + binder + internal standard are pelletized	4	4	0.83
Neutron activation analysis	Counting X-ray at 559 KeV	23	5	0.836

Table 5f - Summary of analytical methods for indium (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + HCl + HF + $HClO_4$; dissolved in 5% HCl	CANMET (2)	10	0.0320
	HNO_3 + HCl + HF + $HClO_4$; tin and arsenic volatilized with HBr; indium extracted into n-butyl acetate from 5 M HBr and back-extracted into H_2O; final solution was 2-5% HCl	CANMET (2)	9	0.0337
	HNO_3 + HF; residue fused with NaOH + Na_2O_2; final solution was 5% HCl	2	5	0.0343
	Indium concentrated by ion-exchange procedure - no other details	14	5	0.0339
X-ray fluorescence	No details	5, 24	8	0.0319
	Loose powder technique	4	4	0.030
Polarography	See above for acid decomposition and indium separation by extraction from 5 M HBr; final solution was 5% HCl	CANMET	4	0.0330
Emission spectrometry	Sample mixed with 4 times its weight of 17.5:2.5 graphite:Na_2CO_3	CANMET	5	0.0363

Table 5g - Summary of analytical methods for bismuth (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + HF + H_2SO_4 + HBr; taken up in dilute HCl; bismuth and iron hydrous oxides co-precipitated; filtered and dissolved in 20% HCl	CANMET (4)	20	0.0323
	HNO_3 + HF; residue fused with Na_2O_2 + NaOH; bismuth + iron + lanthanium hydrous oxides co-precipitated, filtered and dissolved in HCl	2	5	0.029
	HNO_3 + HCl + $(NH_4)_2SO_4$ + H_2SO_4; dissolved in HCl; boiled with $MnSO_4$ and $KMnO_4$ to precipitate bismuth hydrous oxide; filtered and dissolved in 35% HCl	15	5	0.0267
	HNO_3 + HCl; taken up in 5% HCl	17	5	0.033
	HNO_3 + HF + $HClO_4$; taken up in 20% HCl; BiH_3 generation	19	5	0.0370
	HNO_3; no other details	20	5	0.0315
Atomic absorption-graphite furnace	HNO_3 + HF + $NaClO_3$ + $HClO_4$; bismuth precipitated with NH_4OH + NH_4Cl; dissolved in HCl + HNO_3	16	5	0.036
Emission spectrometry	Sample mixed with equal weight of KCl	7	5	0.0338
X-ray fluorescence	No details	5	5	0.0301
	Loose powder technique	4	5	0.026

Table 5h - Summary of analytical methods for molybdenum (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt %)
Atomic absorption	HNO_3 + one or more of HCl, HF, $HClO_4$, HBr, H_2SO_4; final solution was 5-10% HCl containing 1000-2000 mg/L $AlCl_3$	CANMET, 11, 17, 19, 23, 24, 26	35	0.029
	HNO_3 + HCl + HF + Br_2 + H_2SO_4; tin and arsenic volatilized with HBr; dissolved in dilute tartaric acid; molybdenum and tungsten extracted as α-benzoinoxine complex into chloroform from 1.8 M HCl; back-extracted with HNO_3 + $HClO_4$ + H_2SO_4; taken to dryness and dissolved in 15% HCl + 1000 mg/L $AlCl_3$	CANMET	5	0.0288
	HNO_3 + HF + HCl + $HClO_4$; final solution was 10% HNO_3 + 129 g/L KNO_3	15	5	0.0282
	HNO_3; residue treated with HF to remove SiO_2; fused with $LiBO_2$	13	5	0.0302
	HNO_3 + HCl + HF + $HClO_4$; final solution was 20% HCl + Na_2SO_4	3	5	0.0312
	Fused with NaOH + Na_2O_2; taken up in dilute HNO_3	9	5	0.032
Colorimetry	HNO_3 + HCl + HF + $HClO_4$; residue fused with Na_2CO_3; iron + copper removed by double precipitation with NaOH; molybdenum thiocyanate complex	CANMET	5	0.027
Emission spectrometry	Sample mixed with equal weight of carbon	7	5	0.0318
X-ray fluorescence	Loose powder technique	4	5	0.024
	Binder + internal standard pressed into pellets	5	5	0.029

Table 5i - Summary of analytical methods for silver (outliers excluded)

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (µg/g)
Fire assay-gravimetry		26b	5	62.7
Fire assay - atomic absorption	Lead button collection; scorification; parted in HNO_3; complexation with diethylenetriamine	CANMET (2, 3)	15	68.2
Atomic absorption	HNO_3 + one or more of HCl, HF, $HClO_4$; final solution was 10-25% HCl	5, 11, 16, 17 20, 26a, 28	35	70.4
	HNO_3 + HCl + HF + $HClO_4$; complexation with diethylenetriamine; 10% HCl	CANMET	5	68.3
	HNO_3 + HF + $HClO_4$; dissolved in HNO_3 containing 10 g/L tartaric acid	15	5	68.5
	HNO_3 + HF; taken up in 3% HNO_3	19	5	65.7
	$HClO_4$; taken up in 25% HCl	18	5	74.6
	HNO_3 + Br_2 + HF + H_2SO_4; evaporated to fumes of SO_3; silver extracted as bromide complex into chloroform + tribenzylamine from 2 M H_2SO_4 + KBr; stripped with HBr and taken to dryness; taken up in 10% HCl - 1% diethylenetriamine	CANMET	5	67.0
Emission spectrometry	Sample mixed with equal weight of carbon	7	5	76.0
DCP-Emission spectrometry	HNO_3	4	5	73.6

Table 5j - Summary of analytical methods for tungsten

Method	Decomposition, separation, etc.	Lab No.	n	$\bar{x}$ (wt%)
Atomic absorption	HNO_3 + HF; dissolved in 0.5 M KOH	13	5	0.0382
Colorimetry	Fused with $NaHSO_4$; dissolved in tartaric acid; tungsten reduced with $SnCl_2$; determined as W(V)-thiocyanate-diantipyrylmethane complex in chloroform	CANMET	5	0.0440
	HCl + HF + H_3PO_4; iron removed as chloride with isopropylether; tungsten reduced with $SnCl_2$; determined as thiocyanate complex	CANMET	5	0.032
	HNO_3 + HCl + HF + H_2SO_4; silicon volatilized as SiF_4; determined as thiocyanate	9	5	0.042
	HNO_3 + HCl + H_3PO_4 + H_2SO_4 + $HClO_4$; residue fused with Na_2O_2 + Na_2CO_3; tungsten reduced with $SnCl_2$ and determined as toluene 3,4-dithiol complex in n-butyl acetate	14	5	0.049
	Na_2O_2 + Na_2CO_3 fusion; tungsten reduced with $SnCl_2$ and determined as thiocyanate	15, 26	10	0.035
	Na_2O_2 fusion; arsenic removed; tungsten determined as thiocyanate	20	5	0.0448
	HNO_3 + HCl + HF + $HClO_4$; tungsten extracted as tetraphenylarsonium chloride - Anal Chem Acta 30, 501 (1969)	16	5	0.036
X-ray fluorescence	No details	5	5	0.0459
Emission spectrometry	Sample mixed with equal weight of carbon	7	5	0.0294
Neutron activation analysis	Gamma ray count	4	5	0.047

Table 6a - Laboratory results, means and standard deviations for zinc

						MEAN	S.D.
LAB- 4 (XRF)	18.2	18.8	18.6	18.7	18.7	18.6000	.2345
LAB- 5 (AA)	19.09	18.72	19.50	19.23	18.95	19.0980	.2932
LAB- 7 (AA)	19.01	19.16	19.05	19.14	19.02	19.0760	.0695
LAB- 9 (TITR)	19.26	19.31	19.33	19.33	19.28	19.3020	.0311
LAB-11 (AA)	19.0	18.9	18.9	19.0	18.9	18.9400	.0548
LAB-11 (TITR)	19.16	19.16	19.12	19.09	19.20	19.1460	.0422
LAB-12 (AA)	18.86	19.04	19.24	19.27	19.06	19.0940	.1667
LAB-12 (TITR)	19.19	19.02	18.97	19.11	19.13	19.0840	.0882
LAB-14 (TITR)	19.04	19.00	18.99	18.94	18.97	18.9880	.0370
LAB-14 (ICP)	18.4	18.3	18.8	18.7	18.6	18.5600	.2074
LAB-15 (AA)	19.05	19.25	19.10	19.25	19.15	19.1600	.0894
LAB-18 (AA)	19.25	19.50	19.45	19.50	19.40	19.4200	.1037
LAB-19 (AA)	19.1	18.8	19.0	18.9	18.8	18.9200	.1304
LAB-23 (TITR)	19.18	19.15	19.18	19.15	19.14	19.1600	.0187
LAB-26 (AA)	18.80	18.8	18.8	18.8	19.0	18.8400	.0894
LAB-26 (TITR)	18.74	18.79	18.89	18.79	18.89	18.8200	.0671
LAB-28 (AA)	19.2	19.1	19.3	19.2	19.2	19.2000	.0707
LAB-52 (TITR)	19.01	19.01	18.99	18.98	18.98	18.9940	.0152
LAB-53 (TITR)	18.88	18.86	18.92	18.97	18.87	18.9000	.0453

Table 6b - Laboratory results, means and standard deviations for lead

						MEAN	S.D.
LAB- 2 (AA)	4.43	4.42	4.41	4.42	4.38	4.4120	.0192
LAB- 3 (AA)	4.36	4.35	4.35	4.32	4.36	4.3480	.0164
LAB- 4 (XRF)	4.26	4.30	4.22	4.24	4.24	4.2520	.0303
LAB- 5 (XRF)*	3.83	3.57	3.83	3.57	3.83	3.7260	.1424
LAB- 7 (AA)	4.32	4.35	4.36	4.30	4.34	4.3340	.0241
LAB-11 (AA)	4.21	4.22	4.22	4.19	4.20	4.2080	.0130
LAB-12 (AA)	4.27	4.28	4.28	4.26	4.29	4.2760	.0114
LAB-12 (TITR)	4.34	4.37	4.42	4.41	4.39	4.3860	.0321
LAB-13 (AA)	4.27	4.27	4.30	4.30	4.30	4.2880	.0164
LAB-14 (TITR)	4.24	4.19	4.27	4.22	4.30	4.2440	.0428
LAB-14 (ICP)	4.38	4.38	4.41	4.36	4.34	4.3740	.0261
LAB-15 (AA)	4.416	4.401	4.427	4.413	4.404	4.4122	.0103
LAB-17 (AA)	4.28	4.28	4.29	4.29	4.28	4.2840	.0055
LAB-18 (AA)	4.42	4.40	4.45	4.41	4.39	4.4140	.0230
LAB-19 (AA)	4.30	4.30	4.30	4.30	4.30	4.3000	.0000
LAB-24 (AA)	4.32	4.28	4.28	4.24	4.28	4.2800	.0283
LAB-26 (AA)	4.40	4.38	4.38	4.35	4.35	4.3720	.0217
LAB-26 (TITR)	4.33	4.38	4.28	4.28	4.28	4.3100	.0447
LAB-28 (AA)	4.35	4.36	4.35	4.36	4.36	4.3560	.0055
LAB-52 (AA)	4.283	4.300	4.263	4.257	4.264	4.2734	.0178
LAB-53 (AA)	4.35	4.31	4.37	4.32	4.33	4.3360	.0241
LAB-53 (TITR)	4.52	4.54	4.53	4.42	4.50	4.5020	.0482

*Outlying set.

Table 6c - Laboratory results, means and standard deviations for copper

						MEAN	S.D.
LAB- 2 (AA)	1.44	1.42	1.42	1.42	1.42	1.4240	.0089
LAB- 3 (AA)	1.43	1.43	1.44	1.43	1.44	1.4340	.0055
LAB- 4 (XRF)	1.42	1.36	1.40	1.36	1.37	1.3820	.0268
LAB- 5 (AA)*	1.65	1.65	1.60	1.65	1.65	1.6400	.0224
LAB- 7 (AA)	1.42	1.46	1.48	1.44	1.47	1.4540	.0241
LAB- 9 (TITR)	1.42	1.43	1.42	1.43	1.42	1.4240	.0055
LAB-11 (TITR)	1.43	1.44	1.43	1.43	1.43	1.4320	.0045
LAB-11 (AA)	1.45	1.46	1.46	1.46	1.45	1.4560	.0055
LAB-12 (AA)	1.44	1.46	1.47	1.47	1.48	1.4640	.0152
LAB-12 (TITR)	1.43	1.45	1.45	1.47	1.45	1.4500	.0141
LAB-13 (AA)	1.44	1.43	1.43	1.43	1.44	1.4340	.0055
LAB-13 (AA)	1.43	1.42	1.40	1.40	1.41	1.4120	.0130
LAB-15 (AA)	1.458	1.462	1.461	1.460	1.433	1.4548	.0123
LAB-16 (AA)	1.415	1.403	1.406	1.408	1.413	1.4090	.0049
LAB-17 (ELECTR)	1.46	1.47	1.44	1.49	1.44	1.4600	.0212
LAB-18 (AA)*	1.35	1.38	1.35	1.36	1.35	1.3580	.0130
LAB-19 (AA)	1.45	1.44	1.44	1.45	1.44	1.4440	.0055
LAB-20 (AA)	1.444	1.441	1.443	1.443	1.446	1.4434	.0018
LAB-23 (AA)	1.431	1.439	1.442	1.440	1.438	1.4380	.0042
LAB-24 (AA)	1.42	1.42	1.40	1.42	1.42	1.4160	.0089
LAB-26 (AA)	1.44	1.43	1.43	1.43	1.44	1.4340	.0055
LAB-26 (TITR)	1.42	1.42	1.42	1.45	1.42	1.4260	.0134
LAB-28 (ELECTR)	1.45	1.46	1.45	1.46	1.46	1.4560	.0055
LAB-28 (AA)	1.45	1.46	1.44	1.45	1.45	1.4500	.0071
LAB-52 (AA)	1.431	1.437	1.424	1.421	1.426	1.4278	.0063
LAB-53 (AA)	1.47	1.47	1.43	1.45	1.44	1.4520	.0179
LAB-53 (COLOR)	1.44	1.45	1.42	1.45	1.44	1.4400	.0122

*Outlying set.

Table 6d - Laboratory results, means and standard deviations for tin

						MEAN	S.D.
LAB- 2 (AA)	1.27	1.26	1.30	1.27	1.28	1.2760	.0152
LAB- 4 (XRF)	1.24	1.24	1.26	1.22		1.2400	.0163
LAB- 5 (XRF)	1.16	1.15	1.14	1.18	1.14	1.1540	.0167
LAB- 7 (XRF)	1.13	1.17	1.21	1.20	1.18	1.1780	.0311
LAB-12 (AA)	1.34	1.40	1.44	1.33	1.39	1.3800	.0453
LAB-12 (COLOR)	1.30	1.37	1.37	1.40	1.33	1.3540	.0391
LAB-14 (TITR)	1.46	1.33	1.47	1.46	1.44	1.4320	.0581
LAB-14 (ICP)	1.27	1.31	1.29	1.26	1.29	1.2840	.0195
LAB-17 (AA)	1.37	1.34	1.31	1.33	1.34	1.3380	.0217
LAB-20 (XRF)	1.253	1.253	1.246	1.261	1.243	1.2512	.0070
LAB-20 (AA)	1.259	1.257	1.262	1.255	1.254	1.2574	.0032
LAB-26 (AA)	1.28	1.30	1.30	1.27	1.29	1.2880	.0130
LAB-30 (AA)	1.33 1.31	1.32	1.30	1.33	1.28	1.3117	.0194
LAB-52 (AA)	1.282	1.274	1.277	1.251	1.262	1.2692	.0126
LAB-52 (TITR)	1.264	1.246	1.255	1.246	1.255	1.2532	.0075
LAB-53 (AA)	1.289	1.279	1.222	1.269	1.298	1.2694	.0277
LAB-53 (TITR)*	1.02	1.10	1.06	1.02	1.11	1.0620	.0427

*Outlying set.

Table 6e - Laboratory results, means and standard deviations for arsenic

						MEAN	S.D.
LAB- 2 (COLOR)	.863	.860	.869	.869	.865	.8652	.0039
LAB- 4 (XRF)	.82	.82	.84	.82		.8250	.0100
LAB- 5 (XRF)*	1.16	1.16	1.16	1.16	1.17	1.1620	.0045
LAB- 9 (TITR)	0.804	0.804	0.798	0.804	0.798	.8016	.0033
LAB-12 (AA)	0.92	0.90	0.86	0.86	0.86	.8800	.0283
LAB-12 (TITR)	0.83	0.83	0.82	0.83	0.83	.8280	.0045
LAB-13 (TITR)	0.80	0.80	0.81	0.80	0.81	.8040	.0055
LAB-15 (ICP)	0.850	0.828	0.838	0.842	0.836	.8388	.0081
LAB-16 (AA)	0.906	0.897	0.899	0.884	0.882	.8936	.0103
LAB-17 (COLOR)	0.82	0.80	0.79	0.78	0.81	.8000	.0158
LAB-19 (AA)	0.87	0.86	0.92	0.88	0.88	.8820	.0228
LAB-23 (NAA)	0.840	0.833	0.837	0.835	0.837	.8364	.0026
LAB-24 (COLOR)	0.94	0.88	0.88	0.88	0.90	.8960	.0261
LAB-26 (TITR)	0.815	0.815	0.800	0.808	0.815	.8106	.0067
LAB-28 (TITR)	0.82	0.82	0.82	0.84	0.83	.8260	.0089
LAB-52 (COLOR)	0.779	0.775	0.776	0.775	0.772	.7754	.0025
LAB-53 (TITR)	0.85	0.81	0.84	0.83	0.80	.8260	.0207
LAB-53 (COLOR)	0.86	0.89	0.85	0.85	0.79	.8480	.0363

*Outlying set.

Table 6f - Laboratory results, means and standard deviations for indium

						MEAN	S.D.
LAB- 2 (AA)	.0345	.0340	.0340	.0340	.0350	.0343	.0004
LAB- 4 (XRF)	.030	.029	.030	.031		.0300	.0008
LAB- 5 (XRF)	0.0303	0.0299	0.0297	0.0282	0.0296	.0295	.0008
LAB- 7 (ES)*	.0390	.0400	.0385	.0405	.0390	.0394	.0008
LAB-14 (AA)	.0340	.0336	.0340	.0336	.0344	.0339	.0003
LAB-24 (XRF)	0.035	0.036	0.037			.0360	.0010
LAB-30 (AA)	0.0313	0.0319	0.0319	0.0330	0.0324	.0321	.0006
LAB-30 (AA)	.0335	.0333	.0337	.0333		.0335	.0002
LAB-30 (POLAR)	0.0326	0.0329	0.0340	0.0324		.0330	.0007
LAB-30 (ES)	.0350	.0380	.0365	.0345	.0375	.0363	.0015
LAB-52 (AA)	0.0344	0.0337	0.0341	0.0335	0.0336	.0339	.0004
LAB-53 (AA)	0.030	0.034	0.030	0.031	0.033	.0316	.0018

*Outlying set.

Table 6g - Laboratory results, means and standard deviations for bismuth

						MEAN	S.D.
LAB- 2 (AA)	.028	.028	.030	.030	.029	.0290	.0010
LAB- 4 (XRF)	.028	.026	.027	.024	.027	.0264	.0015
LAB- 5 (XRF)	0.0296	0.0303	0.0295	0.0300	0.0309	.0301	.0006
LAB- 7 (ES)	.0340	.0330	.0335	.0340	.0345	.0338	.0006
LAB-15 (AA)	0.0244	0.0274	0.0278	0.0254	0.0287	.0267	.0018
LAB-16 (AA)	0.035	0.036	0.036	0.036	0.037	.0360	.0007
LAB-17 (AA)	0.032	0.033	0.034	0.033	0.032	.0328	.0008
LAB-19 (AA)	.0384	.0372	.0366	.0357	.0369	.0370	.0010
LAB-20 (AA)	0.0314	0.0313	0.0314	0.0318	0.0316	.0315	.0002
LAB-30 (AA)	.0335	.0325	.0318	.0329	.0333	.0328	.0007
LAB-52 (AA)	.0318	.0324	.0321	.0320	.0320	.0321	.0002
LAB-52 (AA)	.0314	.0320	.0319	.0327	.0316	.0319	.0005
LAB-53 (AA)	.031	.032	.032	.034	.033	.0324	.0011

Table 6h - Laboratory results, means and standard deviations for molybdenum

						MEAN	S.D.
LAB- 3 (AA)	0.031	0.031	0.032	0.031	0.031	.0312	.0004
LAB- 4 (XRF)	.024	.025	.024	.023	.024	.0240	.0007
LAB- 5 (XRF)	0.0294	0.0293	0.0283	0.0284	0.0289	.0289	.0005
LAB- 7 (ES)	.0316	.0318	.0316	.0320	.0318	.0318	.0002
LAB- 9 (AA)	0.032	0.031	0.033	0.033	0.033	.0324	.0009
LAB-11 (AA)	0.032	0.032	0.031	0.032	0.030	.0314	.0009
LAB-13 (AA)	0.0301	0.0302	0.0301	0.0302	0.0304	.0302	.0001
LAB-15 (AA)	0.0282	0.0276	0.0285	0.0281	0.0285	.0282	.0004
LAB-17 (AA)	0.029	0.028	0.029	0.029	0.029	.0288	.0004
LAB-18 (AA)*	.038	.044	.035	.040	.033	.0380	.0043
LAB-19 (AA)	.0285	.0280	.0279	.0277	.0285	.0281	.0004
LAB-23 (AA)	0.0278	0.0277	0.0285	0.0286	0.0298	.0285	.0008
LAB-24 (AA)	0.028	0.028	0.026	0.028	0.028	.0276	.0009
LAB-26 (AA)	0.032	0.032	0.031	0.032	0.032	.0318	.0004
LAB-52 (AA)	0.0298	0.0304	0.0297	0.0301	0.0296	.0299	.0003
LAB-53 (AA)	0.030	0.028	0.030	0.029	0.027	.0288	.0013
LAB-53 (COLOR)	0.027	0.027	0.027	0.027	0.026	.0268	.0004

*Outlying set.

Table 6i - Laboratory results, means and standard deviations for silver

						MEAN	S.D.
LAB- 3 (FA-AA)	72.7	71.3	71.7	72.7	71.0	71.8800	.7887
LAB- 4 (ES)	69.	72.	75.	75.	77.	73.6000	3.1305
LAB- 5 (AA)	66.	66.	66.	69.	69.	67.2000	1.6432
LAB- 7 (ES)	76.	78.	76.	74.	76.	76.0000	1.4142
LAB-11 (AA)	69.2	67.6	71.8	69.7	68.6	69.3800	1.5627
LAB-15 (AA)	69.0	68.5	68.0	68.5	68.5	68.5000	.3536
LAB-16 (AA)	71.5	71.5	71.4	71.6	71.5	71.5000	.0707
LAB-17 (AA)	69.	69.	68.	69.	68.	68.6000	.5477
LAB-18 (AA)	75.	76.	74.	73.	75.	74.6000	1.1402
LAB-19 (AA)	66.	65.	65.5	66.	66.	65.7000	.4472
LAB-20 (AA)	72.95	73.15	72.80	73.40	73.45	73.1500	.2806
LAB-26 (AA)	72.0	72.0	71.0	71.0	72.0	71.6000	.5477
LAB-26 (FA-G)	63.8	62.7	67.2	59.7	60.3	62.7400	3.0088
LAB-28 (AA)	72.1	71.3	71.2	72.1	71.3	71.6000	.4583
LAB-30 (FA-AA)	64.1	67.0	66.3	64.3	67.1	65.7600	1.4588
LAB-30 (AA)	69.2	68.1	67.6	69.1	67.5	68.3000	.8093
LAB-51 (FA-AA)	66.9	66.5	67.9	67.3	66.5	67.0200	.5933
LAB-52 (AA)	66.7	67.0	66.7	69.6	65.0	67.0000	1.6538

Table 6j - Laboratory results, means and standard deviations for tungsten

						MEAN	S.D.
LAB- 4 (NAA)	.047	.044	.049	.046	.049	.0470	.0021
LAB- 5 (XRF)	0.0477	0.0446	0.0431	0.0459	0.0482	.0459	.0021
LAB- 7 (ES)	.0290	.0294	.0298	.0294	.0296	.0294	.0003
LAB- 9 (COLOR)	0.044	0.040	0.040	0.040	0.044	.0416	.0022
LAB-13 (AA)	0.036	0.036	0.041	0.038	0.040	.0382	.0023
LAB-14 (COLOR)	0.053	0.049	0.048	0.047	0.049	.0492	.0023
LAB-15 (COLOR)	0.038	0.041	0.038	0.036	0.036	.0378	.0020
LAB-16 (COLOR)	0.035	0.036	0.036	0.037	0.038	.0364	.0011
LAB-20 (COLOR)	0.045	0.045	0.040	0.047	0.047	.0448	.0029
LAB-26 (COLOR)	0.035	0.032	0.032	0.029	0.035	.0326	.0025
LAB-52 (COLOR)	0.0436	0.0467	0.0422	0.0417	0.0456	.0440	.0022
LAB-53 (COLOR)	0.031	0.032	0.032	0.032	0.033	.0320	.0007

It should be noted that 95% confidence limits denote that if the certification program were performed 100 times, the overall mean in 95 would fall within the prescribed limits.

The average within-set standard deviation, σ_A, is a measure of the average within-bottle precision as determined by the analytical methods used. The implication exists therefore that a laboratory using a method of average or better reproducibility should obtain individual results for a given certified element with a precision that is at least comparable to the reported value of σ_A.

CRITERION FOR CERTIFICATION

The ratio of the between-laboratory to the within-laboratory standard deviation, σ_B/σ_A, where

$$\sigma_B = \sqrt{\left[\sum_i^k \left(\bar{x}_i. - (\sum_i^k \bar{x}_i.)/k\right)\right]^2 / k-1}$$

is a measure of the quality of the certification data for the reference materials of CCRMP (7). The acceptable upper limit for σ_B/σ_A is 3 for all elements except uranium for which an upper limit of 2 is more realistic.

The criterion for the certification of an element in a reference material is RP, the percentage of sets of results that must be rejected to give a value of σ_B/σ_A equal to or less than the acceptable upper limit. RP should not exceed 10%.

The values of σ_B/σ_A and RP for MP-1a are reported in Table 7. It appears that zinc, lead, copper, tin, arsenic, tungsten, indium and silver but not bismuth and molybdenum can be certified according to the described criteria. For reasons stated below bismuth and molybdenum are being certified in MP-1a. To the contrary, tungsten will not be certified.

DISCUSSION

Table 5 is a summary of a methodological classification of accepted analytical results

Table 7 - Values of σ_B/σ_A and RP for MP-1a

Element	Number of sets of results	σ_B/σ_A All results	σ_B/σ_A Final	RP %
Zn	19	2.21	2.21	0.0
Pb	21	3.22	2.93	4.8
Cu	27	4.30	2.35	3.7
Sn	16	3.16	2.58	12.5
As	17	2.79	2.79	0.0
W	12	3.42	2.87	8.3
In	12	3.49	2.76	8.3
Bi	13	3.79	2.99	23.1
Mo	17	3.78	2.83	17.6
Ag	18	3.19	2.96	11.1

where there is a clear-cut distinction between types of methods in decomposition, separations and determination steps. No attempt was made for any element to detect a statistically significant difference between the overall means of the more popular methods because there was generally not a sufficient number to warrant the test.

Table 8 summarizes the values of the between-laboratories spread given by

$$2(t_{0.975,(k-1)} \sqrt{V[\bar{x}..]}) \times 100\% \bar{x}..$$

and the mean within-laboratory coefficient of variation given by $\sigma_A \times 100\%/\bar{x}..$ for the inter-laboratory program for the 10 elements for both MP-1 and MP-1a. An examination of the between-laboratories spread readily illustrates an appreciable improvement in MP-1a over MP-1 for all elements except indium. In particular, the large decrease in the between-laboratories spread for MP-1a compared with MP-1 noted for tungsten is the main reason this element has a relatively low σ_B/σ_A ratio in MP-1a. The availability of a reference material such as MP-1 is likely one reason for the improved between-laboratories agreement noted for MP-1a.

A comparison of the values of the average within-laboratory coefficients of variation for MP-1 and MP-1a indicates that the elements fall

Table 8 - Between-laboratories spread and within-laboratory coefficient of variation for MP-1 and MP-1a

	Between-lab spread (%)		Average within-lab coeff of variation (%)	
Element	MP-1	MP-1a	MP-1	MP-1a
Zn	1.53	1.09	0.46	0.52
Pb	3.10	1.49	1.19	0.51
Cu	2.99	1.10	0.82	0.71
Sn	8.90	5.79	2.16	1.69
As	5.71	4.38	1.47	1.50
W*	57.09	20.61	7.87	4.65
In	8.86	8.80	2.41	2.39
Bi	16.02	11.86	5.56	2.70
Mo	13.16	8.00	7.62	1.98
Ag	7.30	5.03	1.50	1.60

*W not certified in MP-1

into two groups - one for which the within-laboratory precision has remained essentially the same, and the other for which improvement has occurred. Of the latter, bismuth and molybdenum show the greatest improvement in the within-laboratory precision for MP-1a compared with MP-1. Indeed, the magnitude of this improvement is sufficiently large that in spite of a significant improvement in the between-laboratories agreement, the ratio of σ_B/σ_A is increased to such an extent that RP of $\leq$ 15% cannot be attained. Similar calculations readily illustrate that bismuth and molybdenum meet the criterion of RP $\leq$15% for MP-1 since $\sigma_B/\sigma_A \leq 3$ initially. Therefore, a paradoxical situation exists wherein bismuth and molybdenum were certified for MP-1 but do not satisfy the certification criterion for its replacement, MP-1a, even though the quality of the results from the interlaboratory program is superior with respect to both between-laboratories agreement and within-laboratory precision. Consequently, CCRMP considers it justifiable to waive the certification criterion for these two elements.

Figures 1a-1j, which show the histograms for the elements in MP-1a after removal of outliers, illustrate that a calculation of a consensus value is warranted for all elements except tungsten. The histogram for tungsten clearly shows the lack of any clustering of the analytical results, a fact which leads to the relatively large value of 20.61% for the between-laboratories spread. Indeed, it is only the relatively poor within-laboratory precision that allows tungsten to meet the certification criterion. Therefore, it is the opinion of CCRMP that using the certification criterion for tungsten would lead to an erroneous result and the lack of consensus precludes its certification at this time. The provisional value for tungsten is given in Table 9.

Indium presents a special example where there appears to have been no change in the between-laboratories agreement and the within-laboratory precision for MP-1 and MP-1a. Since the determination of this element is known not to be especially troublesome, it must be concluded

Table 9 - Provisional value for tungsten

Number of laboratories		11
Number of results		60
Overall mean		0.040%
95% confidence limits,	low	0.036%
	high	0.044%
σ_A		0.002%

that it is of minor interest in the routine operation of analytical laboratories. Supporting this is the fact that only six laboratories besides CANMET submitted results for indium. It may be concluded therefore that indium is of only minor commercial importance.

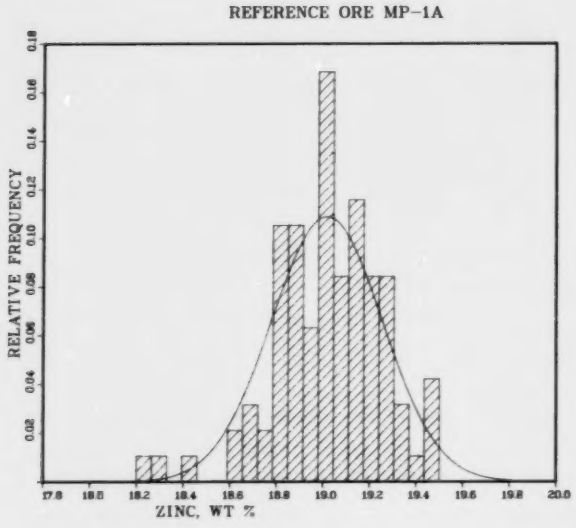

Fig. 1a - Histogram for zinc

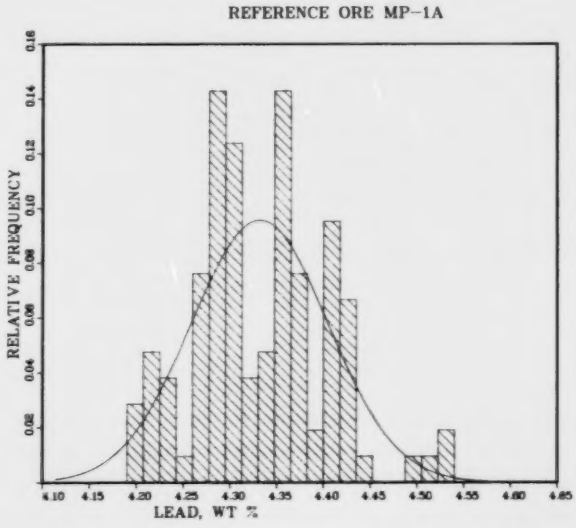

Fig. 1b - Histogram for lead

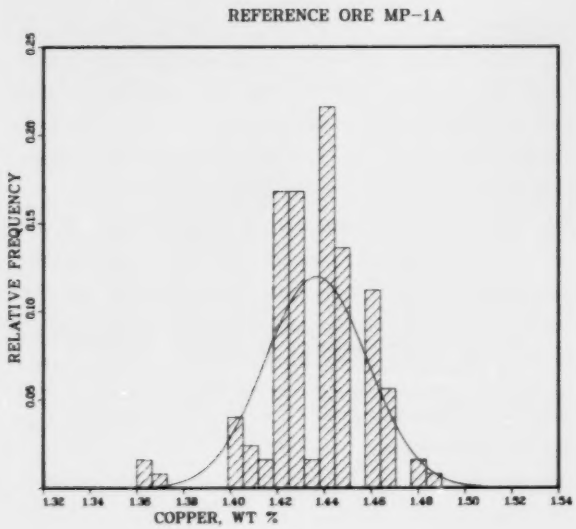

Fig. 1c - Histogram for copper

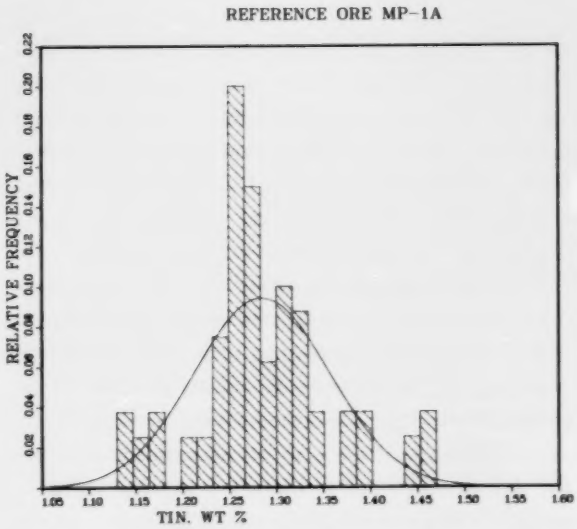

Fig. 1d - Histogram for tin

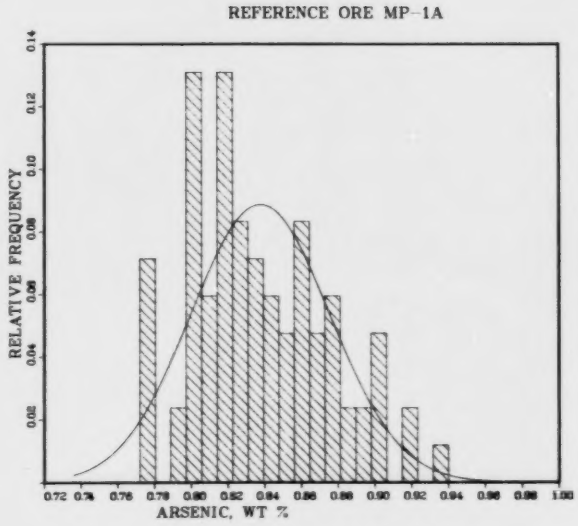

Fig. 1e - Histogram for arsenic

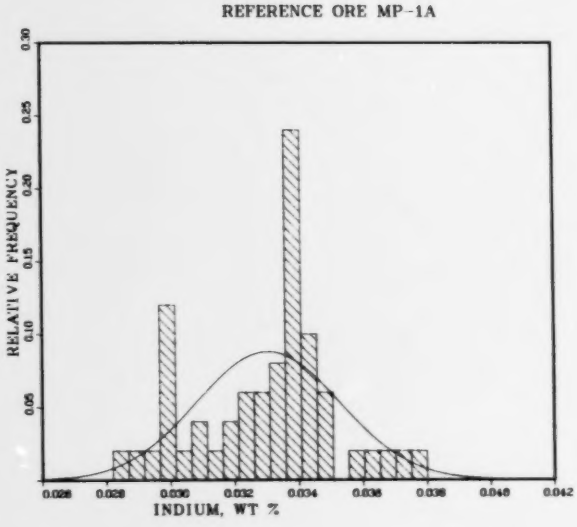

Fig. 1f - Histogram for indium

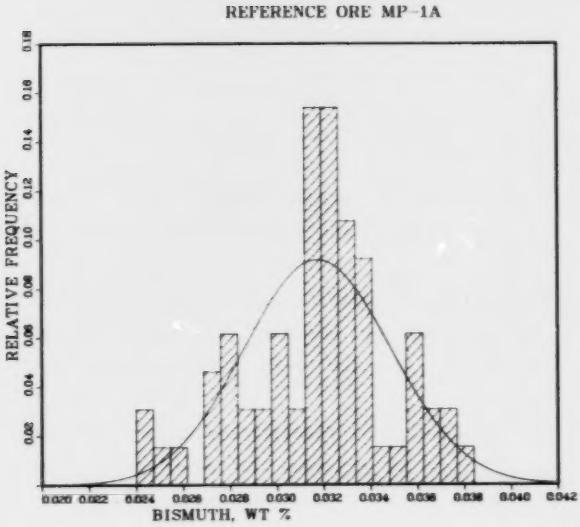

Fig. 1g - Histogram for bismuth

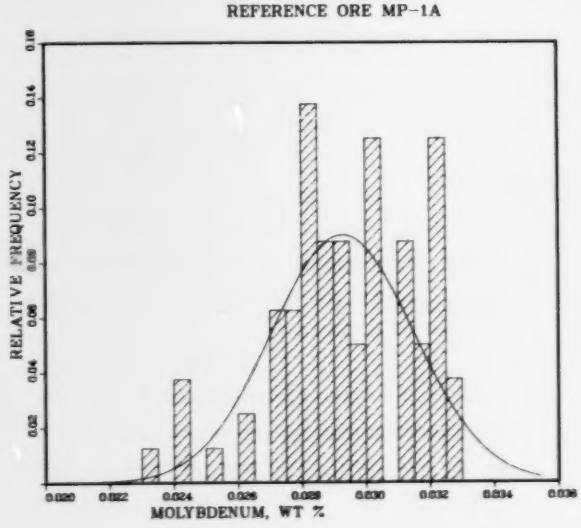

Fig. 1h - Histogram for molybdenum

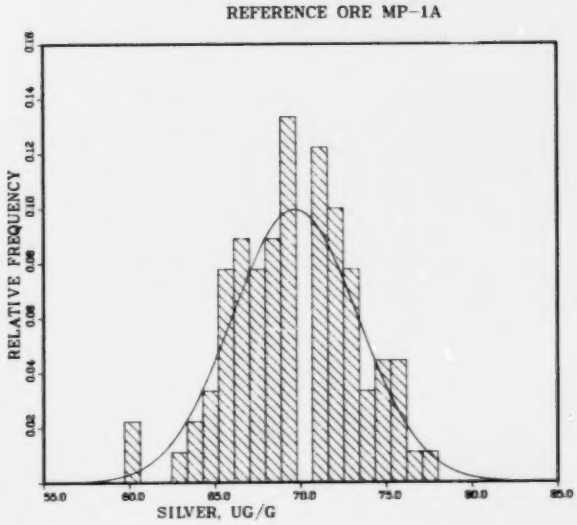

Fig. 1i - Histogram for silver

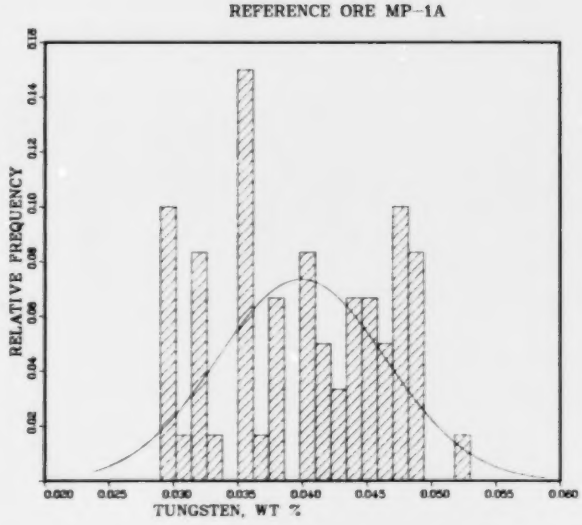

Fig. 1j - Histogram for tungsten

REFERENCES

1. Steger, H.F. "Certified reference materials"; CANMET Report 80-6E; CANMET, Energy, Mines and Resources Canada; 1980.

2. Faye, G.H. "Zinc-tin-copper-lead ore, MP-1: Its characterization and preparation for use as a standard reference material"; Mines Branch TB 155; CANMET, Energy, Mines and Resources Canada; 1972.

3. Faye, G.H. and Bowman, W.S. "Revision of recommended values for reference ores MP-1 and KC-1"; CANMET Report 78-2; CANMET, Energy, Mines and Resources Canada; 1978.

4. Petruk, W. "Field trip to Brunswick Mining and Smelting and to the Mount Pleasant deposit, October 10-20, 1979".

5. Brownlee, K.A. "Statistical theory and methodology in science and engineering"; John Wiley and Sons, Inc., New York, 1960.

6. Steger, H.F. "A re-assessment of the criterion for certifiability in CCRMP"; Geostandards Newsletter VI:17-23; 1982.

APPENDIX A

CONFIRMATION OF HOMOGENEITY

CONFIRMATION OF HOMOGENEITY

The homogeneity of MP-1a was confirmed at CANMET by analyzing in triplicate 15 bottles selected from a stock of 840 for zinc and bismuth. The stock was divided into 15 lots of 56 bottles. The code number of the first bottle was selected at random out of the first lot. The code numbers of the remaining bottles selected were given by the code number of the preceding bottle plus 56. The results are shown in Tables 10 and 11.

A one-way analysis of variance technique was used to assess the homogeneity (5). Herein, the ratio of the between-bottle to within-bottle mean square is compared with the F statistic at the 95% level of probability. No evidence of bottle-to-bottle inhomogeneity was found for either zinc or bismuth.

Table 10 - Confirmation of homogeneity of MP-1a for zinc

	Zn (wt %)			
Bottle No.	Individual			Mean
44	19.08	19.01	19.01	19.03
100	18.96	19.04	18.94	18.98
156	19.00	18.93	18.99	18.97
212	19.06	19.00	18.97	19.01
268	19.02	19.01	19.05	19.03
324	18.97	18.49	18.99	18.98
380	19.01	18.96	18.98	18.98
436	18.97	18.96	18.96	18.96
492	18.98	19.04	18.96	18.99
548	18.98	19.00	18.99	18.99
604	19.00	18.96	19.04	19.00
660	18.96	19.03	18.95	18.98
716	18.99	19.02	18.97	18.99
772	18.97	18.97	18.95	18.96
828	18.97	19.03	18.99	19.00

Overall mean = 18.99

Table 11 - Confirmation of homogeneity of MP-1a for bismuth

	Zn (wt %)			
Bottle No.	Individual			Mean
44	0.0330	0.0313	0.0316	0.0320
100	0.0320	0.0325	0.0322	0.0322
156	0.0314	0.0318	0.0312	0.0315
212	0.0320	0.0317	0.0320	0.0319
268	0.0315	0.0314	0.0309	0.0313
324	0.0327	0.0309	0.0319	0.0318
380	0.0316	0.0316	0.0317	0.0316
436	0.0318	0.0322	0.0324	0.0321
492	0.0324	0.0314	0.0318	0.0319
548	0.0319	0.0318	0.0319	0.0319
604	0.0314	0.0317	0.0315	0.0315
660	0.0327	0.0327	0.0320	0.0325
716	0.0318	0.0312	0.0321	0.0317
772	0.0320	0.0316	0.0318	0.0318
828	0.0318	0.0329	0.0315	0.0321

Overall mean = 0.0318

Analysis of variance table for zinc

Source of variation	Degrees of freedom	Mean square
Between bottles	14	1.232×10^{-3}
Within bottles	30	1.082×10^{-3}
Total	44	

Calculated F statistic = 1.139

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for zinc

Analysis of variance table for bismuth

Source of variation	Degrees of freedom	Mean square
Between bottles	14	2.852×10^{-7}
Within bottles	30	2.173×10^{-7}
Total	44	

Calculated F statistic = 1.312

F.95(14,30) = 2.037

Null hypothesis of no difference between bottles is accepted for bismuth

APPENDIX B

PARTICIPATING LABORATORIES

PARTICIPATING LABORATORIES

Bondar-Clegg and Company Ltd.
North Vancouver, British Columbia
R.K. Rogers

Bondar-Clegg and Company Ltd.
Ottawa, Ontario
P. Haulena

Brenda Mines Limited
Peachland, British Columbia
D. Perkins

CANMET, Energy, Mines and Resources Canada
Mineral Sciences Laboratories
Ottawa, Ontario
(6 independent analysts)

Chemex Labs. Ltd.
North Vancouver, British Columbia
B.L. Twaites

Falconbridge Nickel Mines Ltd.
Metallurgical Laboratories
Thornhill, Ontario
W.L. Ott

Falconbridge Nickel Mines Ltd.
Sudbury Division
Falconbridge, Ontario
R.J. Wiseman

Geological Survey of India
Central Chemical Laboratory
Calcutta, India
A.N. Chowdbury

Geological Survey of West Malaysia, Ipoh,
Perak, Malaysia
Tong Yik Lum

Hudson Bay Mining and Smelting Company Ltd.
Flin Flon, Manitoba
W.W. Henderson

Inco Ltd., Analytical Services
Process Technology
Copper Cliff, Ontario
J. Bozic

Inco Ltd.
J. Roy Gordon Research Laboratory
Sheridan Park, Ontario
St. J.H. Blakely

Lakefield Research of Canada Ltd.
Lakefield, Ontario
D.M. Wyslouzil

National Institute for Metallurgy
Randburg, South Africa
E.J. Ring

Noranda Research Centre
Pointe Claire, Quebec
J.D. Kerbyson

Ontario Ministry of Natural Resources
Geoscience Laboratories
Toronto, Ontario
C. Riddle

Sherritt-Gordon Mines Ltd.
Research and Development Division
Fort Saskatchewan, Alberta
D.J. Whitehead

Sherritt-Gordon Mines Ltd.
Mining Division
Lynn Lake, Manitoba
R. Klassen

Surinam Government Geological and Mining Services
Paramaribo, Surinam
K.E. Burke

United Keno Hill Mines
Elsa, Yukon
V. Rafuse

X-ray Assay Laboratories Ltd.
Don Mills, Ontario
E.J. Brooker